

Thermal and Dynamic Mechanical Properties of Hydroxypropyl Cellulose Films

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Synopsis

Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used to characterize the morphology of solvent cast hydroxypropyl cellulose (HPC) films. DSC results were indicative of a semicrystalline material with a melt at 220°C and a glass transition at 19°C (T_1), although an additional event was suggested by a baseline inflection at about 80°C (T_2). Corresponding relaxations were found by DMTA. A secondary relaxation at -55°C was attributed to the interaction between hydroxyl groups of the polymer and residual diluent. The $\tan \delta$ peak at T_2 was found to arise from an organized phase, presumably from a liquid-crystal mesophase formed while in solution. Crosslinking with a diisocyanate increased the peak temperature of the two primary relaxations, and resulted in a more clearly defined peak for the T_2 transition. From this behavior it was concluded that both T_1 and T_2 are similar to glass transitions (T_g 's) associated with an amorphous component and a more highly ordered phase (due to a residual liquid crystal superstructure) in the HPC bulk.

INTRODUCTION

The observation that hydroxypropyl cellulose (HPC) forms liquid crystal structures in concentrated water solutions was first reported by Werbowyj and Gray.^{1,2} This discovery triggered a wide array of studies into the liquid crystal phenomenon in cellulose and cellulose derivatives,³⁻⁶ which have been reviewed recently by Gray.⁷ Cellulosic liquid crystals are predominantly lyotropic in character, and this necessarily emphasizes the solution behavior.^{8,9} It is important to understand the phase behavior of these polymers in order to judge their material properties in bulk.

This relationship has been greatly advanced by the recognition that a liquid crystal mesophase is formed in the bulk (i.e., thermotropic) of some hydroxypropyl celluloses.^{10,11} Even so, only isolated reports on the thermal behavior of HPC have been published, and they have generally been concerned with the detection of mesomorphic structures. The relationship between the morphology of HPC and its physical properties has not yet been adequately addressed.

The complex morphological order of HPC in bulk was revealed by Samuels,¹² who emphasized crystalline melt behavior. Later studies reported a glass transition (T_g)¹³ at 10°C using inverse gas chromatography, and this was later substantiated in an unrelated study using dynamic mechanical techniques.¹⁴

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In addition, compression-molded samples of HPC revealed a second-order transition by DSC at about 110°C,¹⁵ which has been attributed to a residual nematic phase in the bulk polymer. This is consistent with results by Navard and Hardins,¹⁶ which indicate that the amorphous phase of HPC is actually a low order cholesteric phase, an observation which has been further advanced in light of recent dynamic mechanical studies.¹⁷ These results emphasize the ambiguous nature of HPC morphology in the solid phase.

It is the objective of this work to further characterize the thermal and dynamic mechanical behavior of hydroxypropyl cellulose by varying the preparation conditions to restrict, or enhance, the development of supermolecular morphology in the form of a liquid crystal mesophase. Additionally, the nature of the various relaxation processes in this material are to be addressed through the evaluation of the influence of crosslinking on the temperature at which the transitions are found to occur.

EXPERIMENTAL

Hydroxypropyl Cellulose Films

The hydroxypropyl cellulose used was Klucel 'L,' manufactured by Hercules, Inc. Its nominal molecular weight was 100,000 g/mol, and its molar substitution was given as 4 propylene oxide groups per anhydroglucose unit. Films were prepared by solution casting from dioxane or acetone in Teflon molds. The films were left for 24 h at ambient conditions to allow for solvent evaporation before being removed from the molds and transferred to a vacuum oven. The films were dried under vacuum at 60°C for 1 week and stored over P₂O₅ in a vacuum desiccator.

Crosslinked HPC Films

Hydroxypropyl cellulose films were crosslinked from 10% solutions of either dioxane or acetone cast into Teflon molds. Toluene diisocyanate (TDI) was used as the crosslinking agent with a dibutyl tin laureate (Union Carbide T-9)

TABLE I
Preparation and Characterization of Hydroxypropyl Cellulose Films Crosslinked with Toluene Diisocyanate.

Sample ID	Solvent	Weight ratio TDI/HPC	Network characterization		Transition temperatures	
			Swell (%)	Sol fraction (%)	T ₁ (°C)	T ₂ (°C)
HPC-0	Dioxane	—	—	—	15	70
	Acetone	—	—	—	13	—
	Dioxane	0.025	675.0	23.3	24	70
	Acetone	0.029	1,503.6	36.0	15	—
	Dioxane	0.056	170.9	2.9	26	101
	Acetone	0.056	262.2	7.4	24	80
HPC-10	Dioxane	0.111	90.9	0.5	25	110
	Acetone	0.112	104.6	1.4	30	112
HPC-20	Dioxane	0.200	50.2	0.2	30	130
	Acetone	0.201	63.7	0.3	35	126

catalyst. The cure schedule included 24 h at ambient conditions to allow for solvent evaporation, followed by 12 h at 125°C in a forced-air oven. Formulation details are given in Table I.

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC4 interfaced to the Thermal Analysis Data Station (TADS) was used for thermal analysis with heating and cooling rates of 20°C/min. All samples were run under a purge of dry nitrogen.

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical analysis of the HPC films was performed with the Polymer Laboratories DMTA interfaced with a Hewlett-Packard 9816 micro-computer for data acquisition. A heating rate of 4°C/min was used with a frequency of 10 Hz. Typical sample dimensions were $0.25 \times 1 \times 15$ mm ($t \times l \times w$) in a single cantilever beam geometry.

Swelling Studies

The percent weight gain of diluent and the amount of soluble material of the HPC networks were determined gravimetrically. About 0.5 g of the dry sample was placed in water until an equilibrium weight gain was reached (~ 5 days). After weighing the swollen samples, the material was again dried in a forced-air oven at 100°C for 3 days and reweighed. The degree of swelling and soluble fraction were calculated as follows:

$$\text{swell (\%)} = [(W_s - W_2)/W_2] \times 100$$

$$\text{solubles (\%)} = [(W_2 - W_1)/W_1] \times 100$$

where W_1 is the dry weight of the film before swelling, W_2 is the dry weight after swelling, and W_s is the diluent-swollen network's weight.

RESULTS AND DISCUSSION

Solvent-Cast HPC

Differential Scanning Calorimetry. The most prominent thermal event observed in HPC by calorimetry (Fig. 1) is the crystalline melt, which occurs from 165 to 210°C. Using Samuels'¹² value of $\Delta H_u = 6.44$ cal g⁻¹, the heat of melting for this sample of 0.96 cal g⁻¹ yields a value of 14.4% crystallinity, in excellent agreement with previous reports.^{10,12} It is important to note that a liquid crystal isotropic transition has been reported to occur in this temperature range for HPC of lower molecular weight.¹⁶ Further experiments attempting to resolve this feature were unsuccessful; however, in the absence of X-ray data the possibility that this peak may also result from a cholesteric-isotropic transition cannot be excluded.

The low temperature region of the scan shows a second-order transition at about 20°C, corresponding to the value reported by Aspler and Gray¹³ as the glass transition (T_g) using inverse gas chromatography. Above this event, the

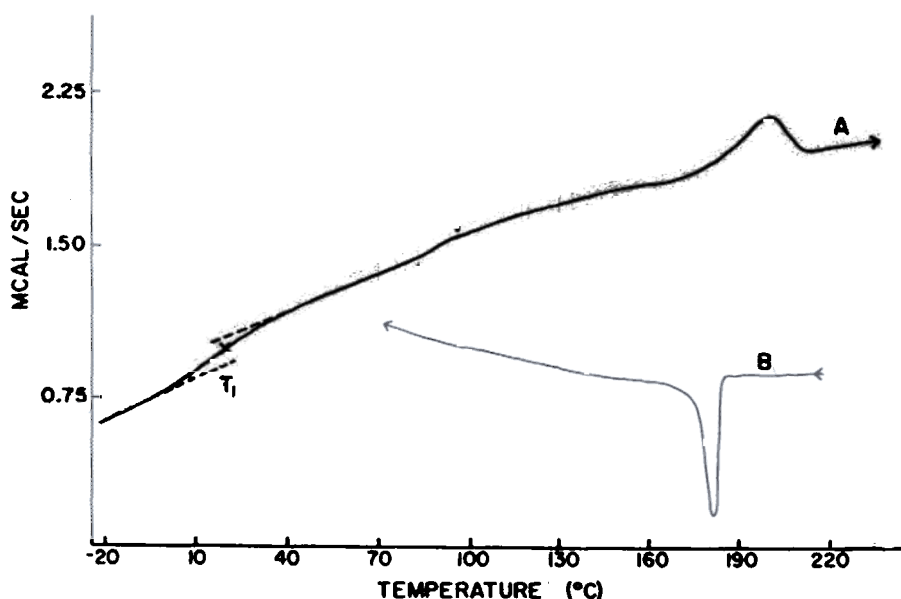


Fig. 1. DSC analysis of hydroxypropyl cellulose cast from dioxane: heating (A) and cooling (B) curves.

material continues a relatively rapid increase in heat capacity (C_p) before plateauing at about 120°C. No additional thermal event is indicated, although a very faint baseline inflection is suggested at about 80°C. A second T_g -like event had been noted in this region for a lower molecular weight HPC.¹⁵

In an attempt to enhance the observed thermal response over this temperature range, the sample was annealed at various temperatures to induce enthalpy relaxation.¹⁸ As seen in Figure 2, a small peak is observed at 75°C after 12 h at 50°C. As the annealing temperature is increased, a small peak occurs at a constant 25°C higher and a relatively constant intensity. Although

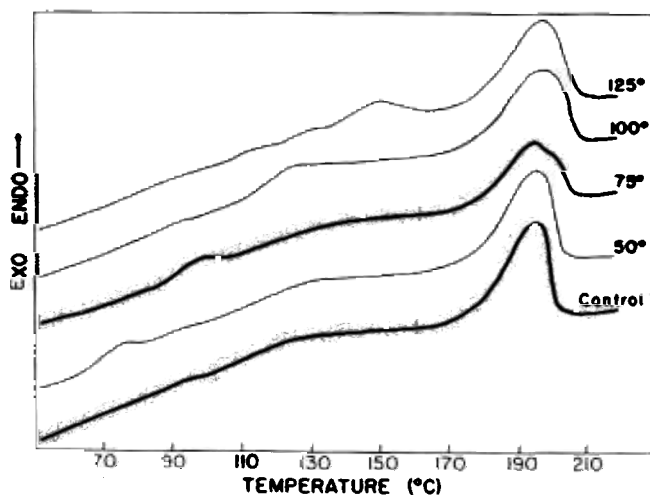


Fig. 2. DSC curves of hydroxypropyl cellulose after a 12 h annealing treatment at the designated temperature.

this is consistent with expected behavior, the response is also induced when the sample is treated at 125°C, which is above the specific event of interest. This observation precludes the assignment of a glass transition by suggesting that the thermal response may be partially influenced by the presence of small, imperfect crystals.

Although inconclusive as to the nature of the observed thermal response in the intermediate temperature region (i.e., 60–130°C), the results on annealed materials suggest the presence of an additional phase in bulk HPC. This finds further support by a more detailed consideration of the glass transition. Of particular interest is the breadth of the transition which occurs over a 50°C range, and the relatively small change in heat capacity that is associated with it. While this is not unusual for a semicrystalline polymer, a more prominent transition would be expected since the degree of crystallinity is relatively low (i.e., 14.4%). In addition, if the T_g of HPC at this composition is estimated from the Fox equation¹⁹ using a T_g of 220°C for cellulose²⁰ and -60°C for propylene oxide,²¹ a value of -5°C is obtained. Since this represents a 25°C discrepancy, this implies that chain mobility may be restricted to a greater degree than expected. A small crystalline phase cannot account for this large difference.

Dynamic Mechanical Thermal Analysis (DMTA). DMTA is generally recognized as being more sensitive to molecular motion, and is, therefore, quite useful for evaluating subtle transitions in polymers. Figure 3 shows the DMTA spectra of hydroxypropyl cellulose cast from dioxane (solid line) and acetone (dashed line). Although obvious distinctions exist, the peaks or relaxation processes in the $\tan \delta$ curve at (1) -60°C (β), (2) 10°C (T_1), and (3) approximately 80°C (T_2) are common to both spectra. It is of considerable interest to identify the origins of these dispersions; particularly, the T_1 and T_2 peaks which involve scale mobility as evidenced by the associated loss in modulus.

The low temperature, β -transition shows little variance between the two spectra, and can readily be attributed to a secondary relaxation process since there is no substantial loss in modulus. Similar relaxation phenomena have been noted in a variety of hygroscopic systems²² and explained as a result of the interaction between diluent (e.g., water) and hydrogen bonding sites in the polymer. In line with this explanation, this process could not be detected in carefully dried samples or, for example, in a second scan of the same sample.

The influence of casting solvent becomes more obvious in the higher temperature relaxations of HPC. The distinction between the two solvents is that HPC forms liquid crystals in dioxane, while mesophase formation is not achieved in acetone.¹³ This explains the observed differences in the dynamic mechanical response between the two HPC films. In the case of the dioxane cast film, the T_1 relaxation appears more as a shoulder on the low temperature side of a broad, but clearly defined, peak (T_2) centered at about 80°C. The acetone-cast film shows a more clearly resolved T_1 peak, while the T_2 relaxation is much weaker and falls off at a lower temperature. This result implies that the T_1 peak arises from an amorphous phase and should be considered as a glass transition in accord with earlier reports.^{13,15}

Analogous observations with regard to T_2 in semicrystalline polymers, i.e., a second relaxation above the material's T_g , have often been ascribed to relaxations in the crystallites.²³ However, no difference in crystallinity was observed

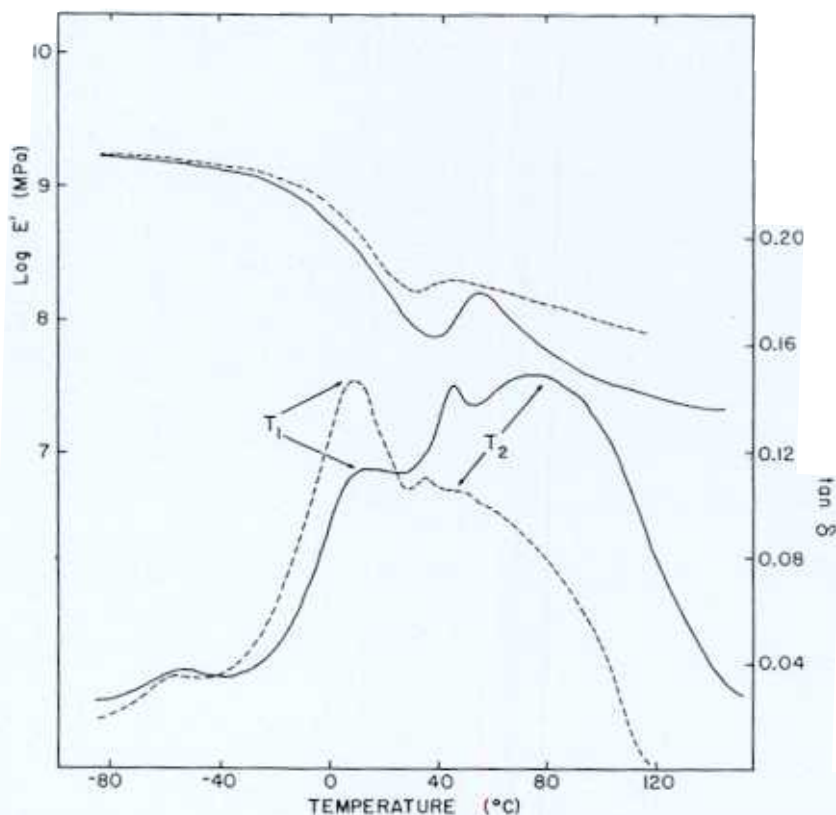


Fig. 3. Dynamic mechanical spectrum ($\log E'$ and $\tan \delta$) of a hydroxypropyl cellulose film cast from dioxane (—) and acetone (---)

between the two samples with estimates of 14.0% and 14.4% obtained by DSC for the acetone and dioxane cast films, respectively. The difference in the intensity and definition of this loss tangent peak has to be the result of a greater extent and higher degree of supermolecular order due to liquid crystal formation in the dioxane solvent. This explanation is consistent with results presented by Charlet and Gray,¹⁷ who associated this relaxation process with the breaking of intermolecular hydrogen bonds. Interestingly, the softening point of this HPC sample determined by thermomechanical analysis is 90°C, suggesting that this residual phase may comprise a significant fraction of the system, contributing to the overall thermal behavior.

Additional information on the nature of these three (β , T_1 , and T_2) relaxation processes can be gained by evaluating the effect of frequency on the peak temperature. Figure 4 shows the Arrhenius plot generated from this experiment using the dioxane cast HPC film. The activation energies derived for the three mechanisms are as follows:

$$\beta (-60^\circ\text{C}) = 62 \text{ kJ mol}^{-1}$$

$$T_1 (10^\circ\text{C}) = 190 \text{ kJ mol}^{-1}$$

$$T_2 (80^\circ\text{C}) = 232 \text{ kJ mol}^{-1}$$

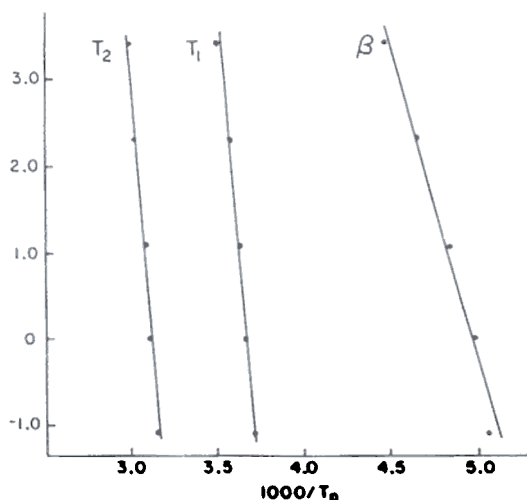


Fig. 4. Arrhenius plot in \ln frequency vs. $1/T_p$ ($\tan \delta$ peak temperature) for the determination of activation energy (E_A).

Although these values concur with the proposed assignments of relaxations, the similarity of the T_1 and T_2 activation energies is surprising. The implication is that similar mechanisms are in effect. That is, both of these relaxations are like glass transitions, involving large-scale segmental mobility in two distinct phases which vary, presumably, in the degree of supermolecular order.

An additional feature of interest in the DMTA spectrum of HPC, Figure 3, is the increase in $\log E'$ that occurs at 40°C. This type of behavior can only be accounted for by three effects: (1) crosslinking, (2) solvent evaporation, or (3) crystallization (for example see Ref. 21). Of these three alternatives, crosslinking and solvent evaporation can be ruled out. Thermogravimetric analysis revealed no weight loss over the temperature range (in question). Thus, this observation must be explained with crystallization. No event is seen in the DSC trace around this point (Fig. 1), but the response could be the result of strain-induced crystallization which would not readily be detected by calorimetry. To further confuse the issue, the occurrence of this modulus rise was inconsistent, and the parameters influencing this response were not successfully isolated. Conceivably, this behavior could arise as a consequence of the test geometry in the event of a substantial sample volume change, although thermomechanical analysis provided no such indication over this temperature region. It is worth mentioning that this same behavior has been observed in ethyl cellulose, ethyl hydroxyethyl cellulose, and cellulose triacetate (Rials, unpubl.).

Crosslinked Hydroxypropyl Cellulose

The temperature at which a T_g occurs can be raised by restricting chain mobility which is easily accomplished by crosslinking.²⁴ This fact can be employed for studying the nature of the relaxation processes in HPC. Table I summarizes the effect of crosslinking agent addition on network structure and both transition temperatures, T_1 and T_2 . The results indicate that T_1 rises

from 13–15°C to 30–35°C; and T_2 rises from 70 to 126–130°C. In addition, swelling and sol fraction correspond well with degree of crosslinking. They are consistently higher for materials crosslinked out of acetone than out of dioxane. This difference may result from a more random distribution of crosslink points in the absence of liquid crystal mesophase formation. As the amount of TDI increases, however, the difference becomes smaller. Also, the amount of light transmission increased dramatically with increased crosslinking in both systems when viewed through crossed polarizers, but it was consistently greater in the films which were prepared using dioxane as the solvent. It appears that crosslinking enhances chain organization in this system.

DMTA of these materials [Figs. 5(A) and 5(B)] reveals similar trends in both solvent series. As the crosslink density increases, the T_2 peak is shifted to

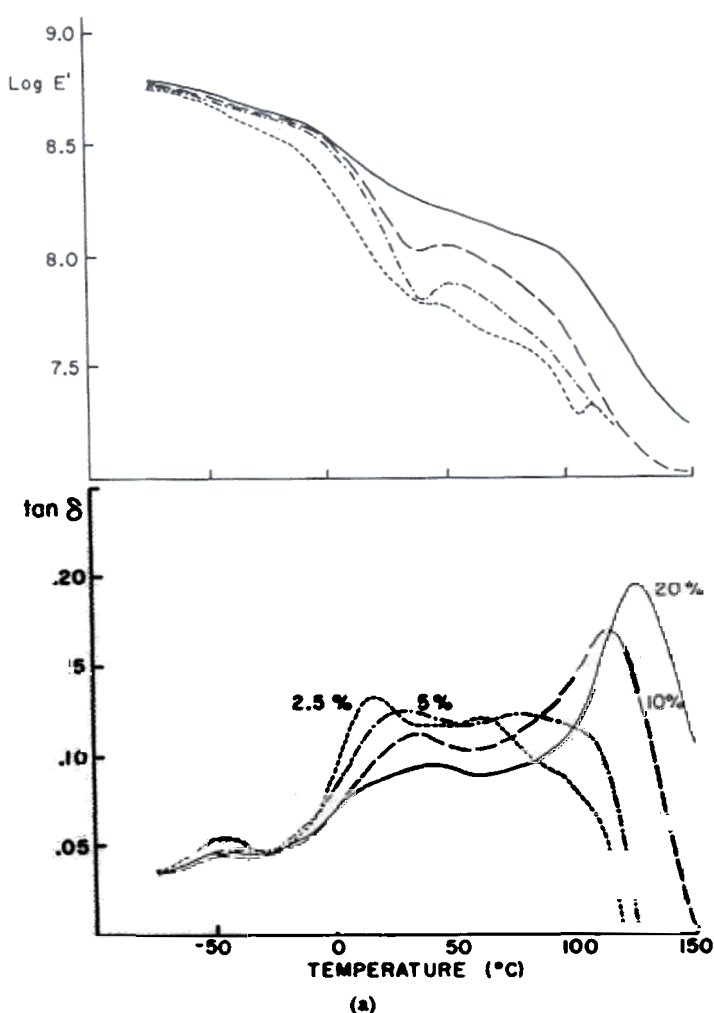


Fig. 5. The effect of crosslinking with toluene diisocyanate on the dynamic mechanical properties of hydroxypropyl cellulose cast from acetone (a) and dioxane (b). The wt % of TDI used in the formulation is presented beside the appropriate curve.

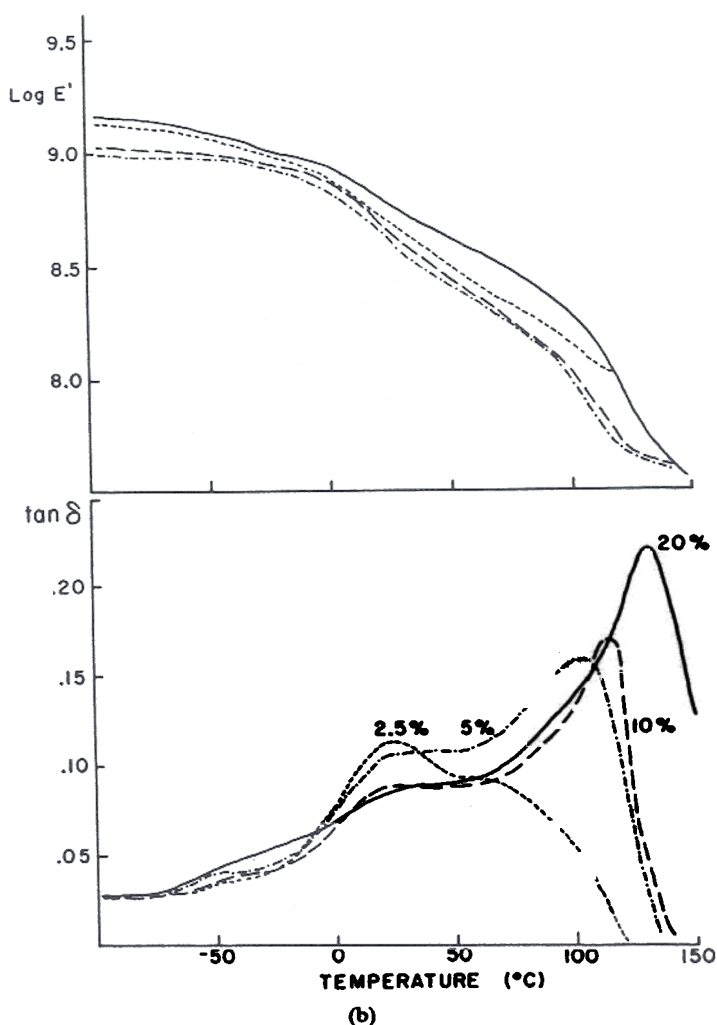


Fig. 5. (Continued from the previous page.)

higher temperatures and greater intensity. The T_1 peak remains much more distinct in the acetone cast films with its maximum occurring at about 5°C higher than that same film crosslinked out of dioxane. However, the important feature of this result is that both primary relaxations, T_1 and T_2 , are shifted to higher temperatures as the degree of crosslinking increases. This implies that these two relaxation processes in HPC resemble a glass transition and arise from two different morphological phases which vary in their degree of order.

CONCLUSIONS

Characterization of the thermal and dynamic mechanical behavior of hydroxypropyl cellulose revealed that this material consists of essentially three distinct phases in the bulk: a crystalline phase, an amorphous phase, and a component which exhibits an intermediate level of order. Both analytical

approaches suggest that this latter phase (arising from the liquid crystal mesophase formed in solution) may constitute a significant volume fraction of the overall system.

The presence of this superstructure was most clearly reflected in the dynamic mechanical properties through two relaxation peaks at about 10 and 80°C, arising from the amorphous and intermediate ordered phases, respectively. As judged by the activation energy associated with the relaxation of these two phases, and the effect of crosslinking on both peak temperatures, it was concluded that a T_g -like transition originates from both phases. This observation is consistent with earlier reports which have indicated the presence of a liquid crystal mesophase in bulk HPC at room temperature.

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